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Photocatalytic α-Oxyamination of Stable Enolates, Silyl Enol Ethers, and 2-Oxoalkane Phosphonic Esters

Peter Schroll[a] and Burkhard König*[a]

Keywords: Photooxidation / Photocatalysis / Radicals / Flow catalysis / Microreactors

Fast α-oxyamination of stable enolates, silyl enol ethers, and in situ deprotonated dialkyl 2-oxoalkane phosphonates and diphenyl-2-oxoalkyl phosphine oxides was performed in the presence of $[Ru(bpy)_3]^{2+}$ (bpy = 2,2′-bipyridyl) as a photocatalyst, 2,2,6,6-tetramethylpiperidine nitroxide (TEMPO), and visible light. The key step was the light-induced one-electron oxidation of TEMPO into the 2,2,6,6-tetramethylpiperidine-1-oxoammonium ion, which was nucleophilically attacked to yield α-functionalized carbonyl compounds. The reaction time was significantly reduced by the use of the microreactor flow technique.

Introduction

Catalytic and stoichiometric one-electron oxidation reactions of different classes of substrates are well established.[1–4] For such oxidations, visible-light photocatalysis has recently been widely applied to provide the necessary redox energy. The photocatalytic oxidation of alkenes by using 9-mesityl-10-methylacridinium perchlorate and subsequent intra- or intermolecular trapping of the resulting radical cation with nucleophiles, such as alcohols, amines, and carboxylates, is an example that was described by Nicewicz et al.[5–9] The generation of carbon-centered radicals $R^{\cdot}$ through one-electron oxidation of borates of the type $R–BX_3^-K^+$ induced by photoredox catalysis followed by reaction with permanent radicals, electron-deficient alkenes, or alkynes was reported by different groups.[10–12]

Enolates and their equivalents are another class of important building blocks in synthetic organic transformations that can be oxidized. Dependent on the oxidant, they yield either an α-carbonyl radical or an α-carbonyl carbenium ion intermediate. With a stoichiometric amount of the weak one-electron oxidant tris-(*p*-methoxyphenyl)aminium hexafluoroantimonate (E = +0.51 V vs. saturated calomel electrode, SCE), α-carbonyl radicals are obtained from stable enolates. Two equivalents of the stronger oxidizing agent tris(1,10-phenanthroline)iron(III) hexafluorophosphate $\{[Fe^{III}(phen)_3(PF_6)_3]$, E = +1.08 V vs. SCE$\}$ afforded α-carbonyl cations as a result of two subsequent one-electron oxidation steps.[13–15] The Jahn group reported the oxidation of ester enolates with $CuCl_2$ or ferrocenium ions and subsequent trapping of the α-ester radicals with 2,2,6,6-tetramethylpiperidine nitroxide (TEMPO).[16–18] All of these reactions allow α-functionalization of carbonyls through an oxidative pathway.

TEMPO catalyzes a variety of oxidation reactions.[19] An important application as reagent is the oxidation of alcohols to aldehydes or carboxylic acids.[20,21] The catalytically active species was found to be the 2,2,6,6-tetramethylpiperidine-1-oxoammonium ion (**2′**, TEMPO$^+$), which is generated in the presence of an oxidant. The oxoammonium ion can react with enolates to give, for example, alkoxyamines.[22] More recently, TEMPO$^+$ was prepared photocatalytically with visible light by using dye-sensitized titanium dioxide and transition-metal complexes based on ruthenium and copper. Following this procedure, the TEMPO-mediated aerobic photocatalytic oxidation of alcohols to aldehydes was reported both heterogeneously and homogeneously.[23–28]

1,3-Dicarbonyl compounds have also been the target of one-electron oxidation reactions[29] and have been used in TEMPO-mediated oxidations with the use of visible light.[30,31] The oxidation of the enol form occurs in the presence of TEMPO (2 equiv.) to afford α-oxyaminated products. However, reaction times of 24–36 h are necessary and different reaction pathways have been proposed considering either a light-induced disproportionation reaction of TEMPO to yield TEMPO$^+$ and TEMPO$^-$ or the reduction of the enol form. We apply now stable enolates in the reaction with photocatalytically generated TEMPO$^+$ to lead to significantly reduced reaction times. The proposed reaction mechanism was supported by control experiments by using different trapping reagents.

Results and Discussion

We started our investigations by treating a 1:1 mixture of stable enolate **1a** with TEMPO (**2**) in the presence of

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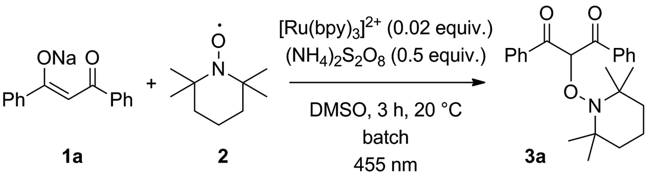
$[Ru(bpy)_3]^{2+}$ (bpy = 2,2′-bipyridyl) as a photocatalyst and ammonium peroxodisulfate as an oxidant. Dry DMSO turned out to be the solvent of choice to dissolve all of the ionic compounds. Irradiation with a blue high-power light-emitting diode (LED, $\lambda_{max} = 455 \pm 15$ nm, $P = 3.0$ W) at ambient temperature afforded desired α-oxyaminated product **3a** in 87% yield (Scheme 1). Control reactions in the dark gave only trace amounts of product **3a**. Without the photocatalyst, a background reaction yielding 4% of α-oxyaminated product occurred. The results exclude efficient direct oxidation of TEMPO by ammonium peroxodisulfate.



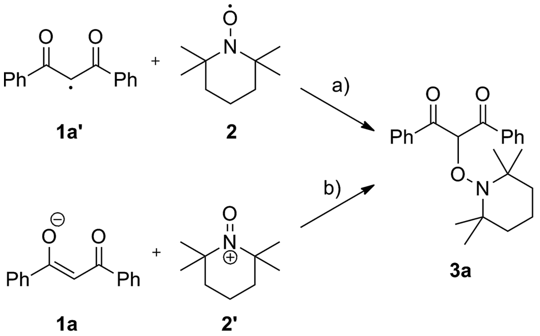
Scheme 1. Photocatalytic α-oxyamination of stable enolates.

Full conversion was achieved after 3 h of irradiation. Hence, the reaction of the enolate was much faster than that of the enol, which required at least 24 h for conversion. By using ammonium peroxodisulfate as the terminal oxidant, the amount of TEMPO could be reduced to 1 equivalent. Without peroxodisulfate, a second equivalent of TEMPO was necessary for full conversion of the enolate. A catalyst loading of 2 mol-% was found to be optimal. Different photocatalysts were screened: Eosin Y gave the α-oxyamination product in 37% yield under green light ($\lambda_{max} = 520 \pm 15$ nm) irradiation. 9-Mesityl-10-methylacridinium perchlorate ("Fukuzumi's dye") as a strongly oxidizing photocatalyst gave the product in 64% yield. However, additional unidentifiable side products were obtained. The product was obtained in 70% yield by using 2,4,6-triphenylpyrylium tetrafluoroborate as the photocatalyst. Both the acridinium and the pyrylium dyes were excited with purple light ($\lambda_{max} = 400 \pm 10$ nm). The best results were obtained with $[Ru(bpy)_3]^{2+}$, which yielded α-oxyaminated product **3a** in 87% yield in a clean reaction. Although enolates are potential ligands for ruthenium ions, the photocatalyst remained stable under these conditions.[32] The reaction time was further reduced by applying flow chemistry in a photomicroreactor. The benefits of flow photochemistry have been discussed through many examples in the literature.[33–37] Compared to the batch reaction, the reaction in a glass capillary offers a larger irradiation surface. By using Equation (1) for the penetration depth l of light, a layer of $l = 1.0$ mm depth contributes to the photoreaction for $\varepsilon = 2.1 \times 10^3\ \mathrm{M}^{-1}\,\mathrm{cm}^{-1}$ and $c = 2.0 \times 10^{-3}\ \mathrm{M}$ in which ε is the molar extinction coefficient and c the concentration of the chromophore $[Ru(bpy)_3]^{2+}$.[38,39]

$$l = (\varepsilon \cdot c \cdot \ln 10)^{-1} \qquad (1)$$

All of the reaction mixture was exposed to light upon pumping the solution through the irradiated glass capillary of 0.5 mm radius (for further details, see the Supporting Information). Switching from batch to a microreactor setup therefore shortened the reaction time from 3 h to 10 min and increased the yield of the α-oxyaminated product to 93%. Despite the fact that oxygen was an appropriate oxidant for the reaction, the sealed conditions in the microreactor demanded ammonium peroxodisulfate as a nongaseous electron acceptor.

The α-oxyaminated product may be obtained by two different reaction pathways: (a) oxidation of the enolate to the α-carbonyl radical followed by radical recombination with the TEMPO radical or (b) TEMPO oxidation and subsequent nucleophilic attack of the enolate (Scheme 2).[22] The structure of the product allows no distinction between the two reaction pathways.

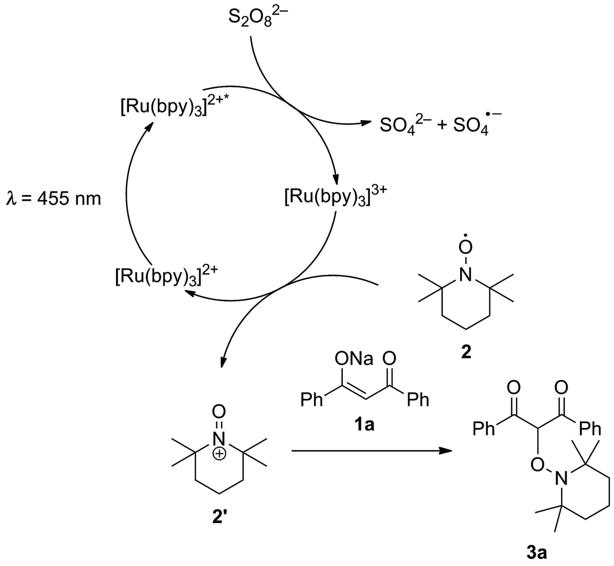


Scheme 2. Generation of α-oxyaminated 1,3-dicarbonyls by (a) radical recombination or (b) nucleophilic attack of the enolate to the oxoammonium ion.

The oxidation potentials of enolate **1a** and TEMPO (**2**) were determined by cyclic voltammetry to be +0.61 and +0.68 V versus SCE in DMSO, respectively. Both cyclic voltammograms show an irreversible oxidation wave (see the Experimental Section). The potentials of the enolate and TEMPO are identical within the error of the measurement and both lie within the photocatalyst's oxidizing ability. Distinction as to which compound is photooxidized is therefore not possible.

However, considering the reactivity of the postulated intermediates, the two mechanisms should be different. In the case of enolate oxidation to the corresponding α-carbonyl radical, other radical trapping reagents should be applicable. Therefore, different π- and σ-electron donors were added to the enolate, but no coupling product was observed with styrene, furan, thiophene, *N*-methylpyrrole, or dimethyl disulfide (5 equiv. each). Moreover, no dimerization product resulting from radical recombination of two α-carbonyl radicals was detected. Even if a catalytic amount of TEMPO (10 mol-%) was added to initiate the oxidation, no reaction was observed with the exception of a small amount of α-oxyaminated product corresponding to the amount of TEMPO added. The presence of TEMPO is essential for the reaction. The absence of any addition product of a postulated α-carbonyl radical and π- or σ-electron donors or the formation of radical dimerization products indicates the one-electron oxidation of TEMPO to the corresponding $TEMPO^+$ ion as the key step of the reaction.

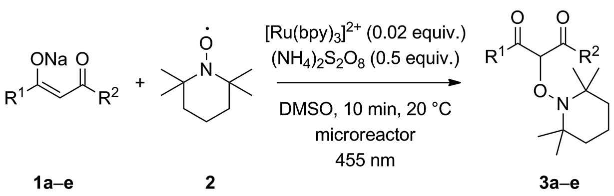
On the basis of these results, the following mechanism is proposed: After excitation of the photocatalyst by blue light, ammonium peroxodisulfate acts as an oxidative quencher to form the strongly oxidizing species $[Ru(bpy)_3]^{3+}$.[40] The oxidant is reduced to sulfate and a sulfate radical anion that is capable of accepting an additional electron.[41] Regeneration of the photocatalyst is achieved by oxidizing TEMPO (**2**) to corresponding oxoammonium ion **2′**. Finally, enolate **1a** attacks the oxidized species in a nucleophilic manner to produce α-oxyaminated product **3a** (Scheme 3).



Scheme 3. Proposed mechanism for the α-oxyamination of stable enolates.

Stable enolates are easily accessible from 1,3-diketones by deprotonation with sodium hydride in diethyl ether at room temperature. Under these conditions, the (*Z*)-enolate is formed selectively.[42] A range of enolates were tested in the α-oxyamination reaction (Table 1).

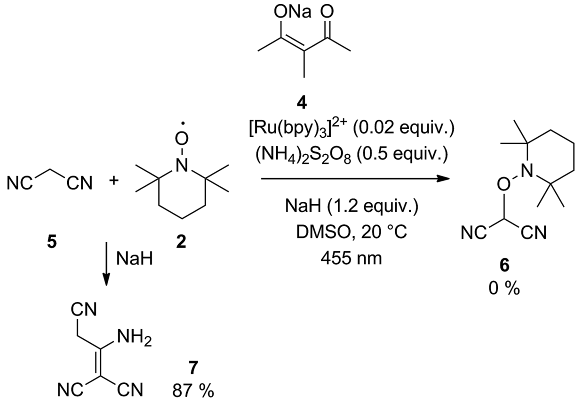
Table 1. Photooxidation reaction of stable enolates with TEMPO.[a]



Entry	Reactant	R^1	R^2	Product	Yield [%]
1	**1a**	Ph	Ph	**3a**	93
2	**1b**	Ph	Me	**3b**	81
3	**1c**	Me	Me	**3c**	82
4	**1d**	Ph	OEt	**3d**	96
5	**1e**	Me	OEt	**3e**	86

[a] Reaction conditions: Enolate (0.6 mmol), TEMPO (0.6 mmol), $(NH_4)_2S_2O_8$ (0.3 mmol), $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (0.012 mmol), DMSO (6.0 mL, absolute), photomicroreactor, irradiation with eight high-power LEDs (λ_{max} = 455 ± 15 nm, P = 3.0 W). Yields of the isolated products are given.

The α-oxyamination proceeded smoothly with 1,3-diketo- and β-keto ester enolates **1a**–**e**. The scope of the reaction was limited to β-keto enolates without substitution at the α-carbon atom: enolate **4** is more basic, which led to decomposition in DMSO solution before irradiation was started. The same applied to enolates of simple aldehydes and ketones, and this limits the scope of the method. Malononitrile **5** did not afford the oxyaminated product. In the presence of a strong base, self-condensation occurred instead, which resulted in the formation of 2-amino-1,1,3-tricyanopropene dimer **7** (Scheme 4).[43,44]

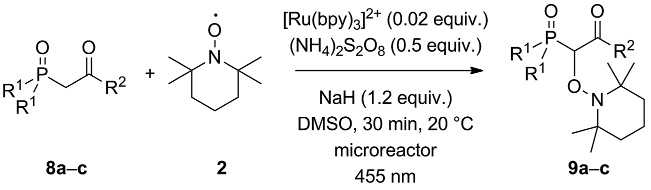


Scheme 4. Limitations in the oxyamination reaction.

According to the mechanistic proposal (Scheme 3), the enolate reacts as a nucleophile. Oxyamination was therefore expected to proceed also with other nucleophiles. To prove the hypothesis, other classes of nucleophiles were examined in the reaction with photocatalytically generated $TEMPO^+$. The nucleophiles were selected by using Mayr's nucleophilicity scale.[45–48]

The principle of α-oxyamination of carbon nucleophiles was extended to β-keto phosphine oxides and β-keto alkyl phosphonic esters. After preparing the enolate in situ by treatment with sodium hydride, nucleophilic attack to the photocatalytically generated oxoammonium ion occurred. Product **9a** could only be identified in trace amounts, but compounds **8b** and **8c** gave desired products **9b** and **9c** in yields of 68 and 57 %, respectively. The reaction time was 30 min (Table 2).

Table 2. Oxyamination of organophosphorus compounds.[a]

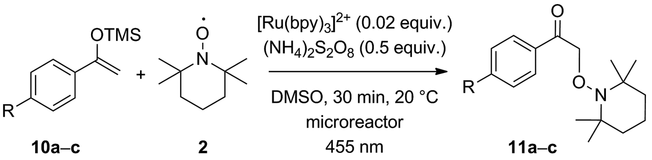


Entry	Reactant	R^1	R^2	Product	Yield [%]
1	**8a**	Ph	OEt	**9a**	trace
2	**8b**	Ph	Ph	**9b**	68
3	**8c**	EtO	Ph	**9c**	57

[a] Reaction conditions: Organophosphorus compound (0.6 mmol), NaH (0.72 mmol), TEMPO (0.6 mmol), $(NH_4)_2S_2O_8$ (0.3 mmol), $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (0.012 mmol), DMSO (6.0 mL, absolute), photomicroreactor, irradiation with eight high-power LEDs (λ_{max} = 455 ± 15 nm, P = 3.0 W). Yields of the isolated products are given.

Enamines have already been successfully used in oxyamination reactions. After hydrolysis, α-functionalized carbonyls were obtained.[49,50] Therefore, related silyl enol ethers were examined as nucleophilic carbonyl derivatives.[51] These enolate equivalents were converted in 30 min under photooxidation conditions into α-oxyaminated products **11a–c** in good yields (Table 3).

Table 3. Oxyamination of silyl enol ethers.[a]



Entry	Reactant	R	Product	Yield [%]
1	**10a**	Me	**11a**	64
2	**10b**	H	**11b**	65
3	**10c**	Cl	**11c**	77

[a] Reaction conditions: Silyl enol ether (0.3 mmol), TEMPO (0.3 mmol), $(NH_4)_2S_2O_8$ (0.15 mmol), $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (0.006 mmol), DMSO (3.0 mL, absolute), photomicroreactor, irradiation with eight high-power LEDs (λ_{max} = 455 ± 15 nm, P = 3.0 W). Yields of the isolated products are given.

Conclusions

A fast and efficient visible-light-mediated oxyamination procedure of β-keto enolates was developed. The method was suitable for α-oxyamination of stable enolates, silyl enol ethers, β-keto phosphine oxides, and β-keto alkyl phosphonic esters. The reaction proceeded through light-induced one-electron oxidation of 2,2,6,6-tetramethylpiperidine nitroxide, which was followed by attack of the nucleophile; this led to α-functionalized carbonyls. The scope of the method was limited by the basicity of the enolate, as basic compounds decomposed under the reaction conditions. The use of flow chemistry in a photomicroreactor reduced the reaction time significantly.

Experimental Section

General Procedure for Photocatalytic α-Oxyamination Reactions of Stable Nucleophiles: A 10 mL flask was equipped with $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (9.0 mg, 0.012 mmol, 0.02 equiv.), nucleophile (0.6 mmol, 1.0 equiv.), TEMPO (93.8 mg, 0.6 mmol, 1.0 equiv.), ammonium peroxodisulfate (68.5 mg, 0.3 mmol, 0.5 equiv.), and dry DMSO (6.0 mL). The mixture was transferred to a glass microreactor (115 × 60 × 6 mm, diameter of capillary: 1.0 mm) by a syringe and was irradiated with an array of eight blue high-power LEDs (λ_{max} = 455 ± 15 nm, P = 3.0 W) for 10 min. The temperature in the microreactor was kept at 20 °C. After that, the mixture was diluted with water (5 mL) and extracted with diethyl ether (3 × 5 mL). The combined organic layer was concentrated in vacuo. Purification of the crude product was achieved by flash column chromatography (petroleum ether/ethyl acetate, 19:1). α-Oxyamination reactions of organophosphorus compounds differ by initial addition of sodium hydride (50 mg, 0.72 mmol, 1.2 equiv., 60 % suspension in paraffin oil) and reaction times of 30 min.

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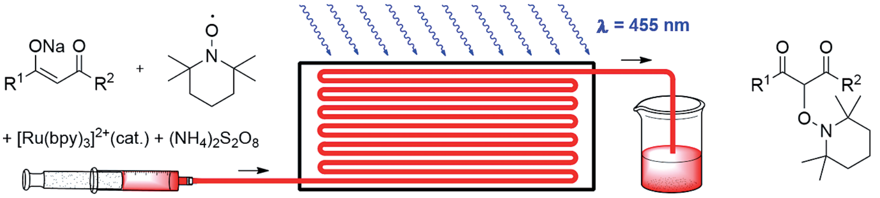
Photocatalysis



Fast and efficient visible-light-mediated α-oxyamination of β-keto enolates, silyl enol ethers, and deprotonated dialkyl 2-oxoalkanephosphonates occurs in a microreactor in the presence of $[Ru(bpy)_3]^{2+}$ (bpy = 2,2′-bipyridyl) as a photocatalyst, 2,2,6,6-tetramethylpiperidine nitroxide (TEMPO), and blue light. The key step is the light-induced one-electron oxidation of TEMPO.

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